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A REVIEW AND PROPOSAL OF OILY AND BILGE WATER TREATMENT USING MEMBRANE FILTRATION TECHNOLOGY

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CONTRACTOR REPORT
Prepared for

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EXECUTIVE SUMMARY

In response to increasingly stringent environmental regulations the Canadian Navy has chosen to replace the currently fitted SAREX coalescing Oily Water Separation (OWS) System with a more robust and effective system. After reviewing the available technologies Director General Maritime Engineering Project Management / Director Marine System Support 4 concluded that a membrane based OWS system would provide the best solution for bilge water treatment. Accordingly, after soliciting bids from various companies a contract has been let with Water Technologies International of Burlington, Ontario to provide 16 such systems to the Canadian Navy over the next three years.

While a membrane based system can meet all naval (compactness, automation and operational effectiveness) and environmental requirements it is anticipated that some difficulties will be encountered in placing a new system aboard HMC Ships. Thus, it is prudent to study the system in order to identify and understand its optimal performance and attempt to anticipate any difficulties that may be experienced with its operation. To optimize the system performance the following parameters warrant study: membrane pore size, operating pressure, cross-flow velocity, the frequency and level of backpulse pressure and cross-flow velocity surges. The effects of temperature and the presence of fine particles in the bilge water are also to be studied. It is anticipated that the major shortcoming with a membrane based OWS will be caused by oil and grease fouling the membrane. While it may be possible to reduce the risk of fouling the membrane will still foul. Accordingly an effective cleaning regime should be developed. This regime could include chemical and/or mechanical cleaning.

With the proper understanding of the capabilities and limitations associated with a membrane based OWS system the Canadian Navy should be able to adhere to all environmental regulations pertaining to oily water discharge while not being saddled with an operator intensive system. With the proper commitment the Canadian Navy can once again demonstrate its innovativeness and develop a world leading engineering solution to a problem of concern to North American and European navies.

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1.0 Introduction

In an effort to ensure that Canadian warships adhere to the applicable environmental regulations regarding oily water discharge, the Canadian Navy has pursued the acquisition and installation of membrane based bilge water treatment systems. These systems hold the promise of achieving environmental regulations and simultaneously meeting other naval requirements, such as compactness, automation and achieving the required bilge water volumetric reductions set by space limitations aboard Canadian warships.

However, as with any new equipment/system, it is inevitable that technical difficulties will be experienced with these systems due to the specific requirements set forward in the treatment of bilge water and the acquiring of expertise in their operation. Accordingly, it is highly recommended that further testing be conducted to determine the optimal conditions for a membrane based bilge water treatment system. This testing should focus on the system to be delivered to the Navy by Water Technology International of Burlington, Ontario.

The most appropriate allocation of resources would be achieved if testing were targeted towards optimizing the type of membrane technology, system operating pressure, back-pulsing sequences, cross-flow velocity and surges, and cleaning techniques. The effects of temperature and the presence of fine particles in the bilge water are also to be studied.

The overall objective of this study is to increase system performance while reducing membrane fouling and meeting or exceeding environmental discharge requirements.

2.0 Methodology

In accordance with the requirements of contract no. W7707-7-4750/001/HAL the following report entitled Bilge Water Purification Using Membrane Technologies has been prepared. The report has been developed using the following criteria:

a. ensure the technology examined is applicable to the Canadian Navy;

b. ensure the technology will achieve the appropriate environmental regulations; and

c. identify methods of improving the operational life/durability of the system - particularly a system's ability to overcome fouling.

The focus of this report is a state-of-the-art examination of the existing membranes available and a critical review of their applicability.

The main resources used in this study were the national technical libraries, including the Canadian Institute of Science and Technology Information (CISTI), DND technical libraries and the Canadian Inter-University Library System. Approximately 80 applicable articles were found, providing the technical information contained in this report. In addition a number of membrane manufacturers and suppliers were contacted. The Internet was also used as an information resource. It provided the identification of relevant companies, information retrieval, dialogue with companies, institutes and knowledgeable individuals, plus the ability to review patents. The refences are listed in the reference section and a list of applicable companies and Internet Websites can be found in Annex A.

3.0 Problem Definition

Aboard ships, wastes and in particular liquid wastes, collect in a ship's bilges. This resulting "bilge water" has a high degree of oil content, especially bilge water produced in the main machinery spaces, due to leakage of oils and greases from shipboard machinery. In the past this water was allowed to settle in the bilges and was

then pumped overboard by taking a suction from a low point in the bilges; the belief being that gravity separation would produce water clean enough for overboard discharge. However, this method of purifying bilge water is obviously limited and as environmental regulations have become more stringent a reliable shipborne Oily Water Separation (OWS) system must be designed and installed aboard ships. Currently Canadian naval warships have coalescing OWS separators installed - which have had limited success with the treatment of bilge water.

For an OWS to be effective in a marine/naval environment it not only has to meet environmental regulations it also has to address shipborne, and in particular naval, concerns. These concerns can be summarized as:

a. substantial volumetric reductions are required due to limited physical space. This is especially true for the IROQUOIS class of ships;

b. equipment space constraints, again due to the limited physical space; and

c. since this is an ancillary system, direct operator supervision should be limited, i.e. system automation should be optimized.

3.1 Environmental Regulations Pertaining to Oil Discharge

The regulations pertaining to oil pollution within the marine environment stem from two jurisdictions: international - the International Maritime Organization (IMO), and national - the Canada Shipping Act (CSA). These regulations are complex, but a synopsis of them follows [55, 57]; IMO regulations state that:

a. within 12 nautical miles of land - effluent discharged overboard cannot exceed 15 ppm of oil;

b. beyond 12 nautical miles of land - effluent discharged overboard cannot exceed 100 ppm of oil;

and CSA regulations state that:

c. within internal waters plus the Gulf of St. Lawrence, Bay of Fundy and the West Coast inner passage - effluent discharged overboard cannot exceed 5 ppm of oil;

d. within all other Canadian waters (eg: east and west coast fishing zones) - effluent discharged overboard cannot exceed 10 ppm of oil; and

e. within Arctic waters zero oil discharge is permitted.

Therefore in order for ships to transit international waters they must possess an OWS system capable of reducing the oil content of bilge water to at least 15 ppm. Within Canadian waters, excluding the arctic, an OWS system must be capable of reducing bilge water oil content to 5 ppm. Assuming that transits within Canadian waters are fairly short then it would be possible to not discharge bilge water during this interval. Therefore, the most pressing requirement would be to achieve the international standard of no more than 15 ppm oil in the discharged effluent, but it would be highly preferable to also achieve an effluent discharge of no more than 5 ppm oil.

3.2 Naval Requirements

As identified earlier for an OWS system to be practical in a marine, and in particular a naval environment, the system must be capable of achieving various naval concerns in addition to achieving environment regulations.

3.2.1 Required Volumetric Reductions

As stated earlier one of the obvious functions that an OWS system must address is the ability to achieve a high concentration of bilge water in the limited space present on ships. Earlier studies conducted by the Canadian Navy have estimated the average production of bilge water as 2.83 m^3/day [56, also see Annex B]. Additionally the

Canadian Navy has determined that it must be capable of reducing this quantity of bilge water to no more than 8 m^3 over a 30 day period. Furthermore, it is preferred that this quantity not exceed 5 m^3 over a 30 day period [80]. This would require the bilge water to be concentrated by a factor ranging from 10.6 to 17.0 (see Annex B).

Within the Canadian Navy this problem is even more apparent on the IROQUOIS class of ships due to a number of reasons, but primarily due to an increased production of bilge water due to contaminated fuel, from the water compensated fuel tanks, being dumped to the bilge. Accordingly, the average daily bilge water production for IROQUOIS Class vessels is approximately 3.03 m^3. This relates to a concentration factor ranging from 11.4 to 18.2.

It should be noted that the above values were averages taken from a Canadian Navy study [56]. Day to day bilge water production values could vary dramatically for any number of reasons therefore the concentration factors given above should incorporate a safety factor. Based upon a safety concentration factor of 50% an OWS system fitted aboard a Canadian Navy vessel should provide a concentration factor in the range of 15.9 to 27.3.

3.2.2 Equipment Space Constraints

Just as the quantity of bilge water that can be held aboard ships is limited so too is the amount of space available for equipment. This problem is further exacerbated aboard naval combatants as more space must be allocated for naval specific equipment. The current SAREX OWS has dimensions of 1.7m in width, 1.0m in depth, and 1.5m in height [80]. Therefore a membrane system should not exceed this space envelope.

3.2.3 System Automation and Operational Effectiveness

Aboard ships, especially naval combatants, the treatment of bilge water is not a primary responsibility. Accordingly, a ship's crew will not want or be afforded the luxury of spending a great deal of time operating an OWS system. Therefore it is paramount that the system be automated so as to remove the element of operator supervision/control and it must be able to run for reasonable periods of time without requiring operator attention, cleaning, part replacement, etc.

3.3 Summary of OWS System Requirements

A summary of the environmental and naval requirements that a Canadian Navy OWS system achieve, with degree of importance in parenthesis, is as follows:

a. be able to reduce the effluent oil content to no more than 15 ppm (mandatory);

b. be able to reduce the effluent oil content to no more than 5 ppm (highly preferable);

c. achieve a bilge water concentration ranging from 16X (mandatory) to 27X (highly preferable);

d. physical equipment size cannot exceed a width of 1.7m , depth of 1.0m and height of 1.5m (mandatory);

e. the system should be as automated as possible (highly preferable); and

f. the system should be as inexpensive as possible (preferable).

3.4 Various Types of Applicable Technologies

There are a wide variety of technologies which could be used to ensure a "clean" effluent from treated bilge water, including [55]:

a. gravity separation;

b. parallel plate separation;

c. (filter) coalescence; and

d. membrane separation.

Each of these technologies possess numerous advantages and disadvantages, with these being summarized as follows.

Gravity separation works upon the principle that the buoyant (specific gravity) differences between water and oil will cause these two liquids to separate if placed in a tank, given sufficient residence time. However, this is not practical for shipborne applications due to the simple fact that for it to successfully remove oil from bilge water an extremely large tank would be required. As described earlier this is not practical for shipborne applications due to space limitations. As well, the motion inherent to ships would also greatly reduce its efficiency as the oil and water would re-mix.

Parallel plate separators work on the principle of gravity separation. The separation being augmented by the use of numerous parallel plates in the tank. These plates provide a surface for oil drops to adhere to and coalesce together - the larger the oil droplet the greater the speed at which the buoyant difference between oil and water will work to separate the two. While parallel plate separation is a more effective solution than gravity separation it is still not practical for shipborne application for the same reasons - space limitations and it is adversely affected by a ship's motion.

Filter coalescence (SAREX unit) is currently employed aboard Her Majesty's Canadian (HMC) Ships and they can provide an effective method for the separation of oil from bilge water. Their essential fundamental principle is the use of woven fiber cartridges as a coalescing media. These cartridges are oleophilic/hydrophobic and as

bilge water passes through them oil droplets coalesce and are therefore able to be separated from the bilge water. The primary advantage of the SAREX units are that they are compact. However, these units require frequent cartridge replacements as they are easily fouled by bilge water and therefore are very labour intensive.

Membrane separation can provide the greatest degree of oil/water separation compared to the other three technologies mentioned. It is simply a matter of selecting a membrane pore size sufficiently small to not allow for the passage of oil droplets - in fact a membrane based system should be able to easily achieve all the environmental regulations. There are numerous examples of membrane technology effectively treating an oil/water solution, as evidenced by nearly all the papers in the list of references and Annex C. Other advantages of a membrane based system are its low energy consumption, flexibility in operating temperatures and that it can easily be automated [33,39]. However, the disadvantages to membrane separation are cost and difficulties due to fouling caused by oils and solids present in bilge water, which can clog the membrane pores [33]. Therefore if adequate pre-treatment, operating parameters and a cleaning regime for the membranes are developed a membrane based system could achieve all of the naval requirements.

4.0 Physico-Chemical Nature of Bilge Water

The ability to process/treat bilge water is a technically demanding challenge due to the fact that bilge water is not merely oily water. It is contaminated with a wide variety of substances, plus its oil component is often, but not always, emulsified [76,80]. Additionally, it is important to remember that "the composition (of bilge water) is neither stable nor predictable" [76].

To examine the challenge of bilge water treatment the following bilge water characteristics must be understood and addressed:

a. composition;

b. oil emulsification;

c. pH; and

d. temperature.

Again it is important to keep in mind that the following description of bilge water characteristics is merely the result of an average sampling. That is, at any given time the composition of bilge water will vary widely from this average sampling. Variations from the average composition will pose unique problems to an OWS system and therefore it must be designed to accommodate such extremes. The largest variable comes from the oil content of bilge water, as actions such as a lube oil change for diesel equipment can result in substantial influxes of oil into the bilge in very short periods of time. A Canadian Navy study [56] reveals, by photographs of various bilge water samples, that bilge water composition can and does vary greatly.

4.1 Composition

Due to the wide variety of components that make up bilge water plus the fact that its composition will vary from ship to ship and mission to mission it is virtually impossible to accurately determine the composition of bilge water at any given time. The primary components of bilge water are sea (salt) and fresh water, in approximately equal proportions. Bilge water contaminants vary widely, with some of the potential contaminants being: diesel fuel, lubricants and greases, solvents, bilge cleaners, refrigerants, paints, boiler compounds, food products, bacteria, cigarette butts, various solid particles (rust, carbon, scale, pipe insulation) etc.

A study conducted on behalf of the Canadian Navy categorized the components of bilge water as follows [56, 80]:

a. Total Oils and Greases (TOG);
b. Total Suspended Solids (TSS). TSS are defined as solids larger than 0.45 microns in diameter;
c. Total Dissolved Solids (TDS). TDS are defined as solids smaller than 0.45 microns in diameter;
d. detergents; and
e. sea and fresh water.

The average composition of bilge water was determined to be:

a. TOG = 1 284 ppm;
b. TSS = 502 ppm;
c. TDS = 17 735 ppm;
d. detergents = 500 ppm; and
e. water (50% sea, 50% fresh) = remainder = 97.55%.

This method of identifying the components of bilge water is very useful as it effectively identifies the major factors which can affect a membrane. However, it does have one shortcoming in that it does not distinguish between oils and greases. This

would be required, particular for membranes, as greases should pose a much greater detrimental effect to membranes as they are more likely to adhere to and coat the membrane surface, thereby necessitating a greater degree of cleaning. Accordingly, to properly test membranes for their treatment of bilge water grease content should be identified separately from oil and its specific effect on membranes should be noted.

4.2 Oil Emulsions

Oil present in bilge water comprises three distinct phases:

a. free-floating oil;

b. unstable oil/water emulsions; and

c. highly stable oil/water emulsions [15].

The specific size and quantity of the oil/water emulsions are created by a number of factors including: imposed shear (from pumping and pipe runs), concentration, oil-surfactant ratio, interaction with filtering media and of course ship's motion [46]; i.e. oil can become emulsified either by mechanical or chemical effects.

Without emulsification an effluent containing approximately 15 ppm oil relates to oil droplets of approximately 20 microns in diameter and less [55,57].

Mechanical emulsions are formed by pumping bilge water, turbulent flow in piping and any other devices in the bilge system that break up oil droplets into smaller droplets. The size of the oil droplets created by mechanical emulsion varies depending on the amount of agitation created and the composition of the bilge water. It is estimated that mechanical emulsions can create oil droplets as small as 0.5 microns [55]. Mechanical emulsions can be reduced by using slow turning/low shearing positive displacement pumps and by using pipes of sufficient size to avoid excessive agitation and turbulence.

Chemical emulsions are caused by the presence of detergents/emulsifying agents/surfactants present in bilge water. While unfortunate for the treatment of the bilge water these compounds serve legitimate shipborne purposes, including [55]:

a. removal of oil from bilge deck plates and ladders to reduce the risk of fires and personnel injury due to slipping; and

b. cleaning of machinery/parts for necessary repairs/maintenance

and cannot be eliminated from use. It has been found that chemical compounds used aboard HMC Ships cause the most severe emulsions resulting in oil droplets as small as 0.05 microns [55]. Further complicating the issue of emulsions is the fact that the quantity and number of different detergents/emulsifying agents/surfactants present in bilge water will affect the quantity and size of oil emulsions [4].

4.3 pH

As the major component in bilge water is sea and fresh water it is expected that bilge water would be slightly acidic. This is correct as bilge water has an average pH of approximately 6.5 [55]. The pH range of various bilge water samples was not too severe, 5.3 to 7.6. pH is not of concern when dealing with bilge water treatment as all membranes can easily tolerate this pH range.

4.4 Temperature

The temperature of bilge water assumes that of the ambient sea temperature, as ship's bilges are located well below the water line and it is only the ship's external hull which separate the two. Accordingly, the temperature of bilge water can range from 2°C to 35°C, depending on where in the world's ocean a ship may be deployed. Similar to pH, the temperature of bilge water is not beyond the limits of membrane elements.

However, temperature will severely affect the morphology and strength of grease particulates. The deformation of these particulates in the filter cake formed on the surface of the membrane will adversely affect membrane flux.

4.5 Uniqueness of Bilge Water

Due to the high commercial production of oily water (eg: from the automotive industry) and of produced water (oil-water-sand mixture in the petroleum industry) numerous studies have been conducted on the treatment of these solutions. However, limited research has focused on bilge water. While oily and produced waters are in many respects similar to bilge water they are certainly not identical. Applying a system which successfully treats oily or produced water could treat bilge water, however it would be expected that numerous difficulties would be found (eg: excessive fouling rates), similar to the experiences found with the currently fitted SAREX OWS system.

One of the primary unique factors associated with bilge water is that it is not of a uniform composition. As described in section 3.1 the composition of bilge water can vary wildly for a wide variety of reasons. Whereas produced water and especially oily water are quite predictable - they are composed of oil, water and sand (for produced water). This unpredictability is a serious problem for the design of a bilge water treatment system because one aspect in membrane selection is choosing a membrane to separate the various compounds. However, if the solution composition or component quantities are continually changing it is more difficult for a particular membrane to always perform effectively. The main problem associated with this variance in composition is that membrane fouling will increase.

Also, the difference in composition between bilge water and oily or produced water is another factor which dictates a unique bilge water treatment system. As an example, in produced water the presence of sand does present a beneficial effect, as

the sand can result in reduced fouling as the sand will scour the membrane surface removing substances which have adhered to it.

Another unique variable associated with bilge water treatment is the size of the oil droplet/emulsion. As described in section 3.2 oil emulsions can be as small as 0.05 microns. Accordingly it would appear that for membranes the simple answer would be to select a membrane with a sufficiently small pore size. However, the problem with this solution is that the smaller a pore size the lower membrane throughput.

Thus, while oily and produced water treatment system are a good starting point for the design of a bilge water treatment system, without specialization it is doubtful that they will adequately provide the optimal treatment solution. Accordingly, the unanswered questions for bilge water treatment are most likely to be membrane pore size and fouling - or more precisely how to reduce fouling to acceptable limits.

5.0 Membrane Selection

When designing a membrane based OWS the most important piece of equipment selection is that of the membrane - in fact proper membrane selection often eliminates a variety of problems. Once a suitable membrane is chosen the remainder of the system can be configured around the membrane to enhance its performance. For a membrane to be suitable for bilge water treatment it must be able to remove a sufficient quantity of oil, maintain a sufficient throughput (membrane flux) for the quantities of bilge water to be treated and not foul at unacceptable levels (i.e. too quickly). The following membrane characteristics are of importance:

a. porosity - i.e. MF, UF, NF or RO membrane;

b. material - either polymeric (organic) or ceramic (inorganic); and

c. configuration - plate and frame, spiral wound, tubular or hollow fibre.

5.1 Porosity

In order for a membrane to even be considered for use in the treatment of bilge water it must be capable of separating water from the contaminants; i.e. the membrane pore size must be fine enough to allow the water to permeate though it while leaving the contaminants behind. As described in section 3.2 oil droplets present in bilge water, can be as small as 0.05 microns. Thus membrane selection will be based upon the ability to cleanse the bilge water of oil droplets of a size of 0.05 microns and larger.

For this range of particle size ultrafiltration membranes are most appropriate. Ultrafiltration membranes can have pore sizes ranging from approximately 0.001 to 0.1+ microns. This is best portrayed in figure 1 which demonstrates the applicable membrane technologies to treat solutions containing various particle sizes [82]:

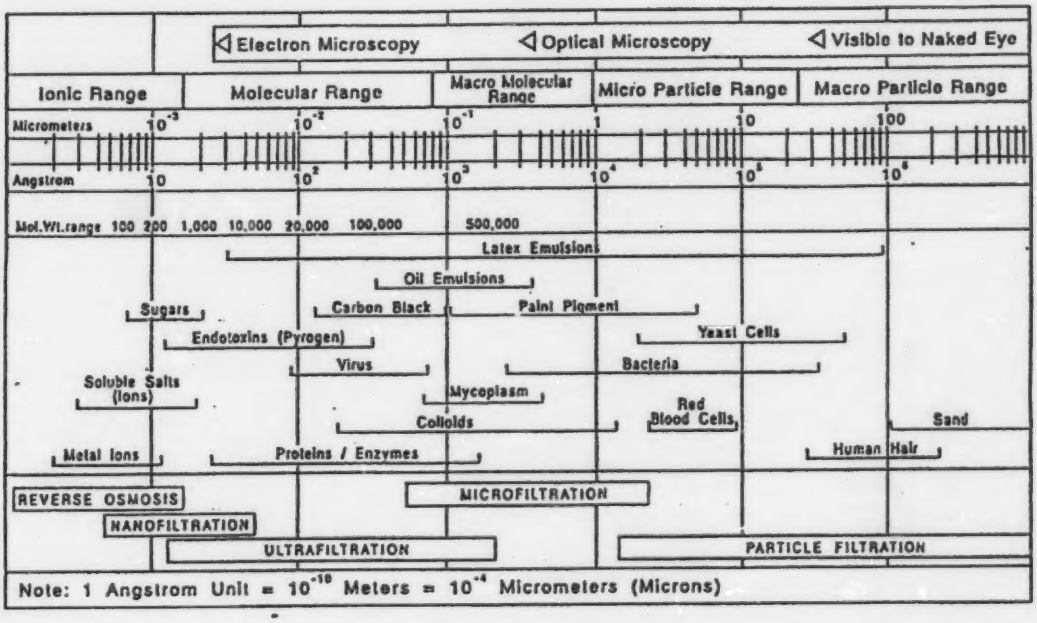

Figure 1: Applications of Membrane Separation Processes

A synopsis of the studies reviewed (Annex C) suggests that to achieve an effluent (permeate) with an oil content of 5 ppm or less it seems necessary that the membrane have a pore size no greater than 0.8 microns (for ceramic membranes) or a molecular weight cut off (MWCO) of 110 000 (for polymeric membranes). However, it must be remembered that these studies were for oily or produced water and probably did not treat heavily emulsified oil as will be the case for bilge water, due to its high ratio of surfactant to total oils and greases plus mechanical emulsion effects. While these studies do not provide us with a reasonable estimate of the pore size required they do give us an indication of the maximum pore size - 0.8 microns or 110 000 MWCO.

To determine the required pore size it would be necessary to identify the distribution of oil emulsions and determine what pore size would limit effluent to 5 ppm. However, as described earlier the composition of bilge water is never stable and therefore it would be moot to determine this distribution. A general rule of thumb is select a pore size one-tenth the size of the particle to be separated [53]. Using this general rule a naval OWS system would require a membrane pore size of 0.005 microns (based on an oil emulsion of 0.05 microns). This corresponds to a molecular weight cut off (MWCO) of approximately 30 000 [53]. Discussion with individuals studying this problem at the USN research facility and at Water Technology International (the successful contractor for the Canadian Navy OWS system) has revealed that they have chosen membrane of 0.0047 microns and a MWCO of 30 000, respectively.

Therefore, membranes with pore size or 0.005 microns are most likely appropriate, however slightly larger pore sized membranes should be tried to determine their success of oil/grease removal. The absolute largest size would be 0.8 microns, but realistically, in the presence of emulsification, the maximum membrane pore size should probably not exceed 0.1 microns.

5.2 Membrane Material

To determine what membrane material type is best suited for bilge water treatment the following factors have been investigated:

a. adequate temperature, pH and pressure tolerance;

b. fouling and flux decline;

c. compatibility with cleaning agents; and

d. compatibility with substances found in bilge water.

Due to the moderate temperatures (2° C to 35° C) and pH (average of 6.5, with a range of 5.3 to 7.6) experienced with bilge water, this is not a factor as both polymeric (organic) and ceramic (inorganic) membranes can easily handle these ranges [16]. Assuming ultrafiltration (UF) membranes are to be employed the system pressure will not be extreme and therefore this also does not differentiate between polymeric or ceramic membranes.

Generally it has been found that ceramic are superior to polymeric membranes for oily water separation as they are generally more chemically, structurally and thermally stable [29, 39].

Numerous studies have all come to the same conclusion that polymeric membranes are much more suspectable to fouling than ceramic membranes and that once fouling occurs ceramic membranes have a greater flux regeneration ability [14, 29, 33, 39, 57, 58, 71]. To help reduce fouling backpulsing/backflushing is generally employed for ceramic membranes [39,71], but does not appear to be appropriate for polymeric membranes [14, 29, 57, 58, 71] resulting from the superior physical integrity of ceramic membranes.

As well, flux decline is much more significant with polymeric membranes than with ceramic. Studies comparing polymeric versus ceramic membranes found that ceramic membranes demonstrate better and more stable permeate flux [39]. During

testing of a Zenon polymeric membrane [58] significant flux declines were noted after periods as short as 72 hours. Further, it was identified that polymeric membranes suffer irreversible flux declines even after cleaning [57, 71] whereas ceramic membranes regain their original flux values after cleaning [71].

Typical cleaning regimes, for both polymeric and ceramic membranes, include a caustic wash, followed by a fresh water wash for the removal of oil and an acid wash, followed by a water wash for solids removal. While both polymeric and ceramic membranes appear to withstand these low concentrations of caustic and acidic washes (non-extreme pH), it is well documented that ceramic membranes have a higher resistance to pH extremes [14, 16, 39, 57]. Ceramic membranes can also be steam cleaned if required, whereas most polymeric membranes cannot [6]. As noted above polymeric membranes do not recover their initial flux after cleanings therefore suggesting some deterioration due to contact with caustic/acidic solutions, or some permanent damage as a result of the contaminants in oily water. In essence polymeric membranes are less robust, durable than ceramic membranes [6].

5.3 Membrane Configuration

Membrane module configurations are varied with each possessing unique advantages and disadvantages. The following are the basic types of membrane module configuration [53]:

a. plate and frame - flat sheet membranes arranged as in a conventional filter press;

b. spiral wound - rolled membranes, where the permeate flows to a central collector tube;

c. tubular - module is packed with a number of membrane tubes. Tubular membranes can have one or several lumens; and

d. hollow fibre (or capillary) - a large number of small (diameter) membranes are packed in a module and the solution flows from the exterior to the interior of the membranes.

In the above discussion of polymeric versus ceramic both membranes were of tubular configuration. The large flow channels associated with a tubular configuration limit the risk of solids clogging the tube inlets [71]. It is this high risk of solids fouling that precludes the use of other membranes configurations such as plate and frame, spiral wound or hollow fibre for use with a solute having high solids concentration. Tubular modules can also withstand reasonably high pressures - important if backpulsing is to be utilized.

Some investigation into the use of non-tubular configurations, such as capillary tubes/hollow fibres, have been proposed for oily water treatment [71]. However, the primary drawback with these configurations is that even with solids pre-treatment the risk of fouling the narrow membrane channels remains high. The advantage with this type of configuration is that a much higher packing density (i.e. higher volumetric capacity) is achievable than compared to a tubular configuration - this would have obvious benefits to a shipborne application. However, due to the high concentration of suspended solids in bilge water it would be difficult to successfully eliminate the risk of fouling from a hollow fibre/capillary tube configuration. Without this serious potential difficulty being overcome and with no proven industrial applications currently available it is very difficult to recommend this type of configuration over tubular.

6.0 Factors Affecting Membrane Performance

The main problem associated with any membrane system is the maintenance of its flux (i.e. membrane throughput). Flux is affected by two prime factors: concentration polarization and fouling. Concentration polarization is the membrane phenomena which results in an increased solution concentration at the membrane surface, compared to the solution's bulk concentration. Fouling occurs as a result of cake formation and pore blockage. Concentration polarization causes a rapid drop in flux, while fouling causes a gradual, long-term deterioration of flux as represented in Figure 2.

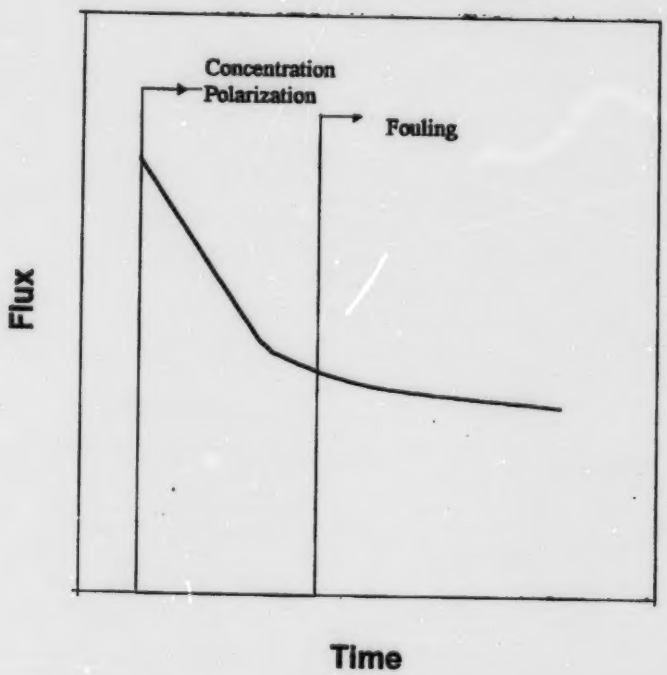

Figure 2: Membrane Flux versus Time [33,54]

The effects of concentration polarization occurs rapidly, within minutes of operation or less, and while it is difficult to quantify this flux decrease it can be reduced by controlling various system parameters including cross-flow velocity, transmembrane

pressure (or the operating pressure for atmospheric permeate discharge), temperature and solution concentration. The most critical factor is cross-flow velocity [33].

The factors which affect concentration polarization also have an effect on fouling. However, the factors affecting concentration polarization are reasonably well known while those resulting in an increase in membrane fouling are not. This is because fouling is often determined by the nature of the solution being concentrated and the membrane used. Accordingly to address fouling it is often necessary to identify the possible foulants present, develop an effective pre-treatment scheme to remove some or all of these foulants and to ensure an effective membrane cleaning regime is developed to counteract the inevitable fouling [33].

6.1 Operating Pressure

System pressure is positively related to the throughput (or flux) of the membrane. That is, as the pressure increases so does flux. However, this positive influence is limited due to diffusive mass transport effects. As stated earlier the solution concentration at the membrane surface is greater than that of the bulk solution. The surface concentration increases with increasing membrane throughput which can be brought about by increasing the operating pressure. Eventually an equilibrium between flux increases and the diffusive mass transfer effects are reached - it is at this point that an optimal transmembrane (operating) pressure is achieved. Figure 3 shows this general relationship between pressure and flux.

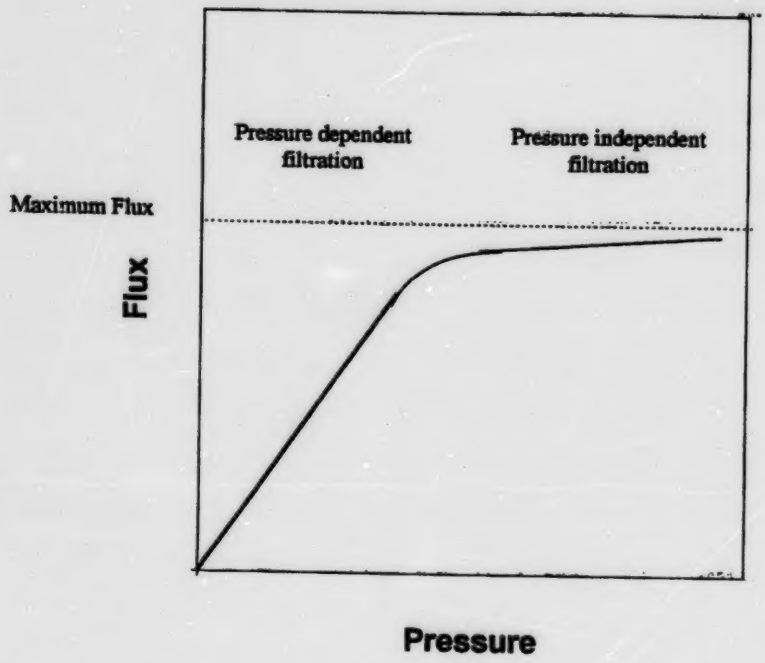

Figure 3: Effect of Transmembrane Pressure on Flux [53,79].

Furthermore, if the operating pressure is too high it could result in an increased rate of fouling [5]. Accordingly it is important to determine the operating pressure which maximizes flux, but does not create too much fouling, which in turn leads to increased cleaning cycles. The optimal transmembrane pressure will likely be in the range of 5 to 45 psi [6, 14, 29, 33].

6.2 Cross-flow velocity

Cross-flow velocity is the velocity at which the bulk feed solution flows across the membrane surface. Generally cross-flow velocity is positively correlated with flux, up to a point where its effect wanes. This effect is represented in Figure 4. The higher the cross-flow velocity the less the differential between a solution's bulk concentration

and its surface concentration which results in a higher flux. A high cross-flow velocity has the added benefit of reducing fouling on the membrane surface [5]. However if the cross-flow velocity is too high the dynamic layer formed on the membrane surface, which acts as a skin layer to further separate the contaminants, can be washed away [14]. Therefore just as for pressure it is important to determine the optimal cross-flow velocity for membrane performance. A reasonable estimate for cross-flow velocity is in the range of 1 to 4.5 m/s [5, 14, 29].

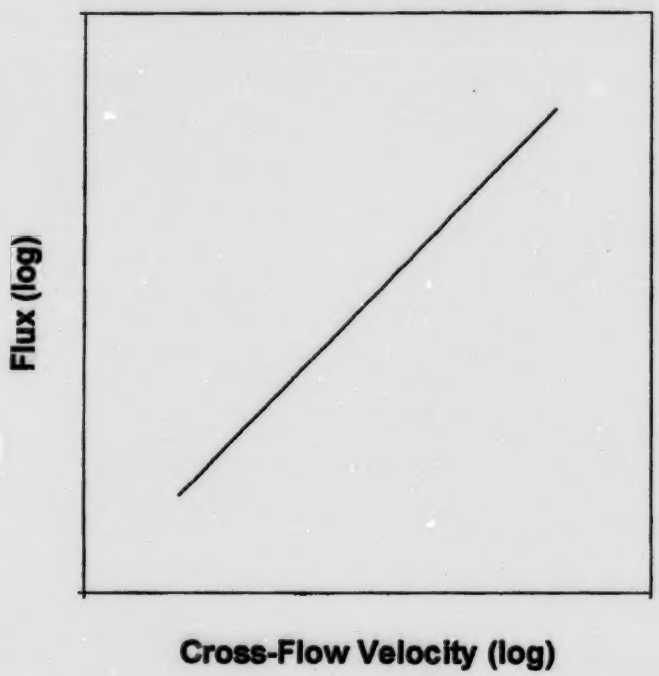

Figure 4: Effect of Cross-flow Velocity of Membrane Flux [53,79]

6.3 Temperature

Unlike pressure or cross-flow velocity the temperature of the bilge water will not be controlled by the system - due to the quantity of bilge water produced this would be

unrealistic and a waste of shipborne energy requirements. However, temperature will have a significant impact on system performance and this effect should be known so that operators do not mistake the reduced/improved performance as being attributable to another factor and try to correct for it. While it is known that temperature will affect a membrane's performance for oily water treatment there are contradictory thoughts about what effect temperature will have.

Generally, temperature increases will result in increased membrane flux. This is because as temperature rises, viscosity decreases and therefore solution more easily flow through a membrane. A general rule of thumb is that flux increases by approximately 3% for every °C [5, 53]. The effect is expressed graphically in Figure 5.

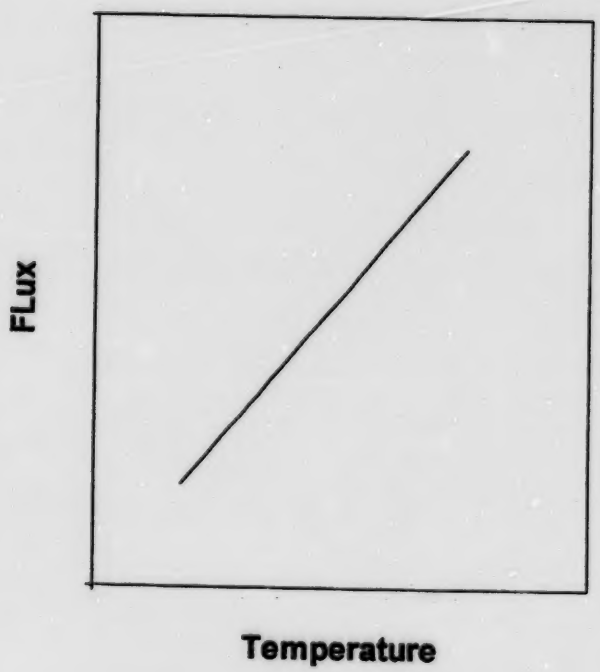

Figure 5: Effect of Temperature on Membrane Flux [79].

However, it has been noted that for oily water solutions increases in temperature will result in reduced separation of oil and water [47]. This seems to occur because as temperature increases the size of oil droplets/emulsions decreases. Accordingly as oil droplet size decreases oil can more readily penetrate into the liquid skin layer on the membrane and result in increased membrane fouling. It has been reported that at temperatures of 35°C fouling increases significantly [47]. However, when the oil in water content is low (10 ppm) it appears that the effect of temperature on flux is as described in general conditions - i.e. temperature and membrane flux are directly related [48]. An additional effect in the treatment of bilge water will be the deformability of the particulates containing greases with temperature. As temperature increases so does the deformability of these grease particulates. Studies on filter cake compressibilities of bilge water will lead to interesting and useful data for the operation of the production scale systems. These filter cake compressibility tests can easily be done in a laboratory using small membrane test coupons.

6.4 Concentration

As a solution's concentration increases its flux through a membrane decreases. For pressure independent filtration, shown in Figure 3, the relationship between concentration and membrane flux is [53]:

$$J = K \ln(C_g/C_b);$$

where: J = membrane flux
C_g = maximum gel (surface) concentration
C_b = bulk solution concentration at large distances away from the membrane surface.
K = mass transfer coefficient

This flux vs. solution concentration (C_b) relationship is described in Figure 6.

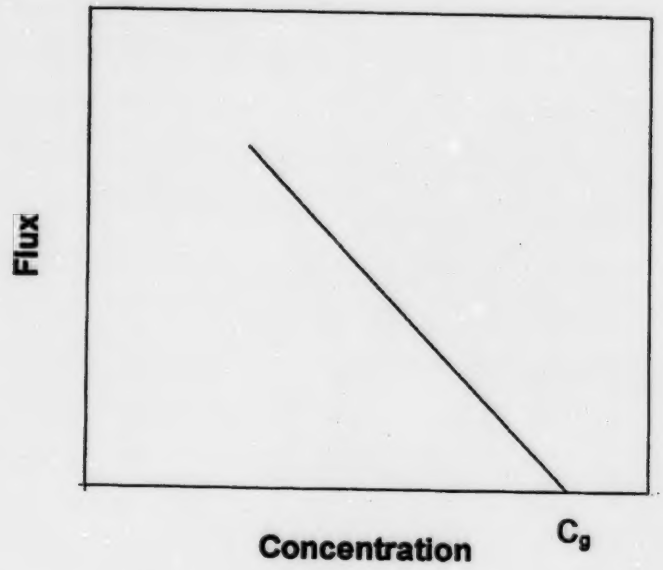

Figure 6: Effect of Concentration on Membrane Flux.

However this is not to suggest that a solution can be concentrated up to this surface concentration level because other factors, such as fouling and precipitation may affect the membrane performance.

For oily waters a concentration of upwards of 60-70% is possible; however concentrations beyond 25-30% appear to result in difficulties associated with membranes fouling [6, 33, 46, 53]. Another study also noted that an oil concentration of up to 30% had no effect on the ceramic membrane - the permeate collected remained "crystal clear" [14].

Directly related to oil concentration is volumetric reduction. It has been revealed that membrane flux is related to the number of volumetric reductions according to the following relationship [48]:

$$J \propto V^x$$

where; J = membrane flux V = volumetric reductions.

Figure 7 graphically represents this relationship.

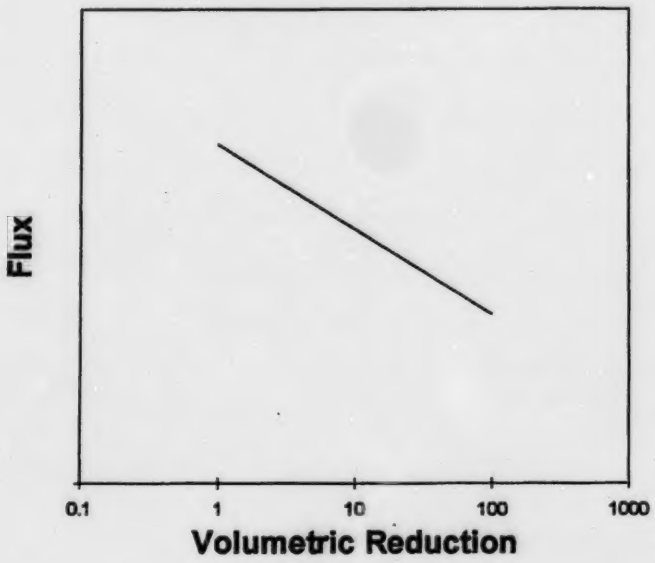

Figure 7: Effect of Volumetric Reductions on Membrane Flux

A study on Membralux ceramic membranes attempted to determine the effects of oil concentration on membranes. Using a feed varying in oil content from 100 to 300 ppm the transmembrane pressure was maintained in the range of 4 to 13 psi while achieving an oil concentration of 60X in the feed. Further concentrations up to 100X resulted in no additional transmembrane pressure increases [14]. However, it is most likely that the maximum allowed volumetric reduction will be governed by the initial bilge water concentration and the maximum oil content that the membrane can tolerate (between 25 -70%) and not flux requirements as the maximum oil tolerance level while likely be achieved before the volumetric reductions begin to impact on the membrane's flux capacity.

6.5 Fouling

While it is certainly important to select the most appropriate membrane and to optimize its operating parameters the rationale behind the selection of these factors is known and can be relatively easily determined. It has been offered that the mechanics behind fouling, due to oily water separation, result from [20, 26]:

a. surfactant adsorption on the pore walls;

b. build-up of a (gel) polarized layer of concentrated oil emulsions at the membrane surface; and

c. pore blockage.

Furthermore for a non-stable solution (such as bilge water) the effects of fouling are noted to be increased [33]. It is expected the greatest impairment to a membrane treatment system will result from the low fluxes achieved due to fouling [47]. The flux reduction due to fouling has been noted to be as high as a 90% reduction after reasonably short periods (6 hours) of operation [20].

Fouling will result due to the non-water components present in bilge water, especially the oils and notably greases. While fouling will not necessarily decrease the membrane performance - initially a dynamic layer will form on the membrane surface resulting in improved separation - certain aspects of fouling will definitely be detrimental.

It is not anticipated that fouling, due to the solids found in bilge water will be a problem for the membranes. If fouling due to solids occurs this should be reasonably easy to correct for through either backflushing and cross-flow velocity surges and/or cleaning (to be discussed later).

However, fouling due to oils and greases will be a serious problem towards membrane operation. Generally, the decrease in membrane flux during the treatment of oily waters results from the membrane being coated with a thin layer of emulsified oil [6]. If a significant quantity of oils or greases contact the membrane surface then the

membrane will undoubtedly become seriously fouled. What are significant quantities of oils and greases? This question unfortunately does not have a definitive answer and it will vary from membrane to membrane. However, it is reasonable to assume that the upper limit will begin to be approached at 25% at which point the fouling risk is greatly increased. For greases the quantity that a membrane could tolerate are quite likely significantly less, due to the nature of greases - if they were to contact a membrane they would be expected to exhibit substantial adherence to the membrane material.

Due to the unpredictable nature of bilge water this will likely lead to increased rates of fouling as it has been found that the less stable a solution the greater the fouling rate [14].

The best method to reduce the severity of fouling is to reduce, and eliminate if possible, high quantities of oils and greases coming into contact with the membrane. A simple, yet effective method, is through effective pre-treatment where the majority of oils and greases are removed from the bilge water prior to it being treated by the membrane (to be discussed in section 6.1).

If, and when, oils and greases contact membranes it is necessary to be able to remove them to regenerate the membrane. This is achieved by an effective cleaning regime (to be discussed in section 7.3). This is a definite advantage of ceramic versus polymeric membranes because ceramic membranes are able to withstand much more rigorous chemicals and therefore can be better cleaned [53,71].

Regardless of what contaminants foul the membrane - oils, greases, or solids - the effect will be an increase in transmembrane pressure. Accordingly, at a certain pressure the membrane will require cleaning. It is anticipated that this pressure will be approximately 30-40 psi [14].

7.0 Increasing Membrane Performance

The previous section described some of the system variables which can affect membrane performance. The goal in optimizing membrane performance was to maintain the membrane's flux. This is achieved by controlling the factors which limit concentration polarization or fouling. Similarly, to increase membrane performance the goal is the same - to limit membrane concentration polarization and fouling. As described concentration polarization is optimized by controlling the various system parameters. Whereas to control fouling it is necessary to limit the membrane's exposure to those components which foul a membrane. This can be accomplished by pre-treatment of bilge water to remove as much of the contaminants, notably free oil and greases, as possible, removing the oil and other contaminants which build up on the membrane and by cleaning the membranes when substantial quantities of oil and other contaminants adhere to the membrane.

7.1 Pre-Treatment

Experience gained from various industrial oily water membrane treatment systems has found that the following pre-treatment actions have the greatest impact on improving membrane performance [33]:

a. free oil removal - this results in an increased membrane flux of approximately 18%; and

b. equalization/residence time - if an oily water solution is allowed to settle for a given period of time this allows free oil to separate from water thereby increasing system efficiency. It was found that increasing equalization time from 0-0.9 to 1-1.9 days resulted in a flux increases of approximately 20%. Further increasing the residence time to 2-2.9 days

resulted in a further flux increase of approximately 16%. There was no further advantage beyond an equalization time of 3 days.

Bilge water pre-treatment can be accomplished in a wide variety of manners. The following are some of the available options, which are considered most practical for bilge water treatment aboard HMC Ships [55,71]:

a. coarse filters;

b. coalescers - parallel plate, ceramic, filter and gravity;

c. hydrocyclones; and/or

d. chemical injection.

A very simple and inexpensive pre-treatment method is to insert a coarse filter prior to the membranes. While it will not be effective for the removal of free oils it is for the removal of large suspended solids (such as fibers, food particles, etc.). This will not only help to maximize other pre-treatment methods and the effectiveness of the membrane modules, it will also prevent damage to the pump(s) in the system.

Both coalescers and hydrocyclones could be utilized for the removal of free oil. In addition to removing the free oil to prevent membrane fouling free oil pre-treatment also allows the OWS to handle possible surges in free oil. While both, coalescers and hydrocyclones, are capable of removing free oil their methods of achieving this are completely different and therefore offer their own advantages and disadvantages.

Coalescers operate upon the principle of using a media of some sort to attract oil droplets together so that they can form larger oil droplets. When the droplets are large enough they become buoyant and separate from the water. There are many different types of coalescers including gravity, parallel plate, ceramic and filter.

Gravity coalescers are a proven method of extracting free oil from bilge water and unlike filter coalescers they are not effected by emulsified oil. They also possess the advantage of being quite inexpensive because they are simply a tank which provides the solute with time to settle whereby the free oil rises to the surface of the

solution and is removed. Their effectiveness is directly related to their size, which is a serious disadvantage as space is a premium aboard ships. Gravity coalescence can be assisted in a number of methods such as the insertion of screens and baffles or introducing unique inlet and outlet positions all with the effect of increasing the residence time of a solute in a given tank size [61]. While this does improve their effectiveness, gravity coalescers will always require a significant amount of space which does not make their use practicable for Canadian warships. However, it would be beneficial to have a small tank, prior to the membrane, where the bilge water would be allowed to settle. The amount of buoyant separation effected by a "small tank" would be directly related to the residence time of the water in the tank, but this would be an inexpensive option.

Parallel plate and ceramic coalescers are essentially modified gravity coalescers and despite the improvements offered over gravity coalescers are still not well suited to shipborne applications because of a ship's continual pitching and rolling motion and the large size required.

Filter coalescers are extremely effective at extracting free oil from bilge water and are not adversely affected by ship's motion. However, when contacted with emulsified oil they become fouled and their effectiveness quickly falls off. Currently HMC Ships are fitted with filter coalescers and this is one of the main difficulties associated with their use [55, 58, 59].

A novel method of achieving oil coalescence is to use a microfiltration membrane to effect the coalescence [17, 26]. This phenomena of oil coalescence through membranes has been documented in fundamental studies of micro/ultrafiltration of oil water emulsion [46, 50], however it does not appear to have been exploited for oil removal from water. For this application the membrane would not be used in the traditional sense; i.e. the solution flowing through the membrane (the permeate) would not be the "clean water" solution. The membrane pores would act as

the coalescing media as oil droplets would contact in the pores. The passage of sufficient oil through the membranes can be achieved by exceeding the normal transmembrane pressure. The distinct advantage of using this type of coalescence are:

a. using a membrane saves physical space;

b. reduction of the different types of technology used in the system;

c. reduction of the quantity of oil seen by the main membrane; and

d. since the membrane would be used to coalesce oil its fouling, by oil, would not be as great a concern.

Hydrocyclones utilize two principles in the separation of free oil from bilge water - a drop in pressure across the unit and centrifugal forces created by the swirling action of the fluid in the hydrocyclone chamber. Hydrocyclones offer a number of distinct advantages over coalescers including: compactness, an ability to handle large volumes of solute quickly and not being affected by oil emulsions or ships motion. As well they are very effective at separating oil down to a droplet size of approximately 25 microns [72]. Their one drawback does appear to be cost; they are significantly more expensive than coalescers (costing approximately $10,000 versus $2,000 for gravity coalescers) [61].

The effectiveness of all of the above described methods are dependent on the oil droplet size distribution in the bilge water. That is, if a high proportion of the droplets are small then the effectiveness of all of the above methods will be lessened. Hydrocyclones will be effected the most as unlike all the other methods they do not attempt to coalesce the oil into larger droplets. Accordingly, limiting the amount of mechanical and chemical oil emulsification is critical to all of these methods - just as it is critical to the currently fitted SAREX OWS system.

Chemical injection is another effective method of pre-treatment. As an example the addition of ferric chloride into produced water minimizes membrane fouling. While

the exact rationale for its success was not specifically identified it is suspected that the ferric chloride created a floc which coated the membrane, effectively acting as a skin layer [71]. While this method could be useful in some applications, it is not viable for shipboard use [80] due to a number of reasons including: ships would have to store the chemical additive, monitor its usage (taking up operator time), it would further complicate the OWS and it is unknown how effective this method would be when affected by ship's motion.

Accordingly, the pre-treatment methods recommended for use in a shipborne OWS are:

a. coarse filters; and

b. hydrocyclones.

Further, the use of a microfiltration membrane to enhance oil coalescence and its removal by the hydrocyclone is recommended for further investigation.

7.2 Backpulsing and Cross-Flow Velocity Surges

Two very effective membrane specific methods of increasing the membranes performance are to have periodic backpulses and surges to the cross-flow velocity.

Backpulsing is the technique whereby at regular intervals a surge of clean water is sent through the membrane in the opposite direction of operation. The purpose of this is to "push off" the particles that have built up on the membrane surface. This procedure should occur whenever the transmembrane (operating) pressure reaches a level at which the membranes are operating outside of their optimal range. Typically, this is done approximately every 2-3 minutes for a 0.5 - 1 second duration with a pressure approximately 2-10X normal operating pressure [29].

Cross-flow velocity surges are applied to "wash away" particles that are on the membrane surface. By applying a cross-flow velocity much greater than the normal cross-flow velocity the particles on the membrane surface can be removed. Typically,

cross-flow velocity surges are 1.33-6X the normal operating cross-flow velocity for a duration of 4-5 seconds [29]. This should be done in conjunction with backpulsing so that the backpulsing pushes the foulants off the membrane and the cross-flow velocity surges "wash" the foulants away.

7.3 Cleaning Regime

The typical cleaning regime for membranes treating oily water is to use a caustic wash for oil removal and an acidic wash for solids removal - both followed by clean water washes to remove the chemicals from the membranes [6, 26, 33, 45]. Cleaning cycles normally take approximately 30 - 60 minutes and occur weekly; although the length and frequency will be dependant on the degree of fouling [6, 33]. This chemical cleaning regime has proven to be very effective, returning membrane flux to their original levels [71]. Again, this reveals another advantage of ceramic over polymeric membranes as ceramic membranes can withstand much stronger chemicals - thereby achieving a better chemical cleaning.

Due to the significant effects fouling can have on membranes significant work has and continues to be done on improving cleaning regimes. One such study found that using sodium dodecyl sulphate and n-pentanol solutions increased the cleaning efficiency due to micellar oil solutions [33]. Other studies have studied the effects/benefits of chemical cleaning using stock "Henkel Ultrasil" products [5, 45]. The alkaline detergent "Ultrasil 11" [5, 45] and acidic "Ultrasil 70" [45] appear to be the preferred cleaning chemicals. An alkaline sodium hypochlorite solution is yet another option as a cleaning chemical [45].

It has been noted that after acidic cleaning the flux is greatly improved, however over time there is a gradual degradation in flux. It has been suggested that this is a result of the acidic cleaning causing the inorganic foulants to become more porous and in the presence of transmembrane pressure these increasingly porous inorganics

become more embedded in the membrane. With alkaline cleaning the flux improves, the effect is not as great as for acidic cleanings. However, there is no flux degradation over time associated with alkaline cleanings. [45]

While chemical cleaning is the most common method for solid and oil cleaning of membranes it is also possible to utilize mechanical cleaning - essentially scrubbing the membranes. An approach used for tubular membranes has been the insertion of sponge balls injected directly into the solution to scrub the inner surface of the tubes. Studies have revealed that this "ball cleaning" does prevent severe flux declines [53]. "Ball cleaning" would have two distinct advantages over chemical cleaning:

a. this cleaning mechanism can be used without interrupting the bilge water treatment process; and

b. no chemicals are required.

However, "ball cleaning" is not practical for all membrane modules due to physical size restrictions.

Another possibility would be the addition of particulates into the feed stream to scour the membrane surface to remove adhered substances. The material would have to be stable and it could either be input initially and remain in the system or added and removed at set intervals. An example of a possible material is fine sand. The advantages to such an approach are its simplicity and very low expense. However, its effectiveness, the possible detrimental effects on the membrane and the modes of particulate recovery, are not well documented.

8.0 System Treatment Scheme

Up to this point in this report we have examined the individual units of a bilge water membrane treatment system without examining how they would work in conjunction with each other. It would be expected that a well designed system operate better than the sum of its parts. As described earlier, a membrane system would require pre-treatment. Additionally it may be worthwhile to have a "polishing step" for the membrane permeate. A membrane having a smaller pore size would be an ideal "polishing" technology as it would be treating a relatively clean water and therefore would not be exposed to the severe fouling conditions associated with the primary membrane.

As discussed in section 7.1 pre-treatment would consist of a coarse filter (to remove the larger solid particles, a hydrocyclone (to remove the free oil) and possibly a microfiltration membrane (to enhance the coalescence and the subsequent removal of oil).

The polishing membrane would have to be a tighter membrane (i.e. have a smaller pore size) than the ultrafiltration membrane. However, a reverse osmosis membrane - which is used in the production of potable water from salt water - would retain all salts. The excessive osmotic pressures of the feed solution on concentration would limit the use of such a membrane to lower recoveries. This would produce a slightly oily brine and may present another disposal problem. Accordingly the pores of the polishing membrane would be required to be sufficiently small to not allow any of the remaining oils and greases to pass, but allow the salt to pass. A very tight ultrafiltration or a nanofiltration membrane would be appropriate.

Accordingly, four basic system configuration could exist:

a. pre-treatment, using a coarse filter and a hydrocylcone, followed by ultrafiltration membrane treatment;

b. pre-treatment, using a coarse filter, hydrocyclone and a (coalescing) microfiltration membrane, followed by ultrafiltration membrane treatment;

c. pre-treatment, using a coarse filter and a hydrocylcone, followed by ultrafiltration membrane treatment and a polishing membrane; and

d pre-treatment, using a coarse filter, hydrocyclone and a (coalescing) microfiltration membrane, followed by ultrafiltration membrane treatement and a polishing membrane.

A configuration without pre-treatment would not be practical as it is a certainty that pre-treatment is required to prevent the chances of a surge of oil/grease being seen by the membrane. Accordingly Figures 8 and 9 are schematic diagrams of the proposed configurations.

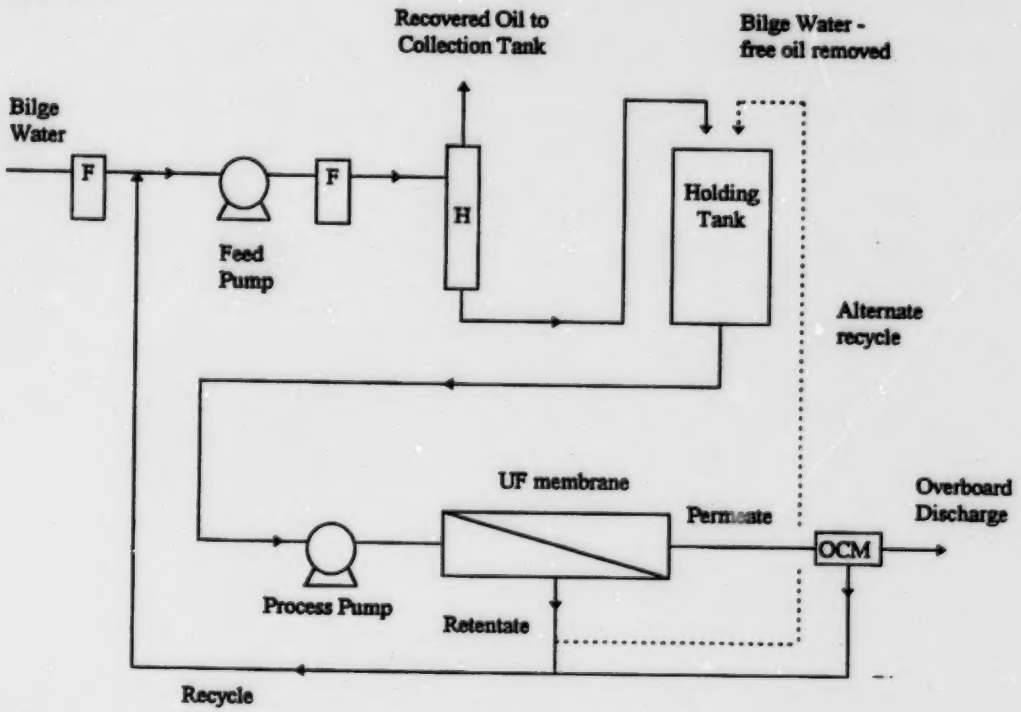

Figure 8 OWS System with Hydrocyclone Pre-treatment. H- Hydrocyclone, F-coarse filters OCM- oil content monitor.

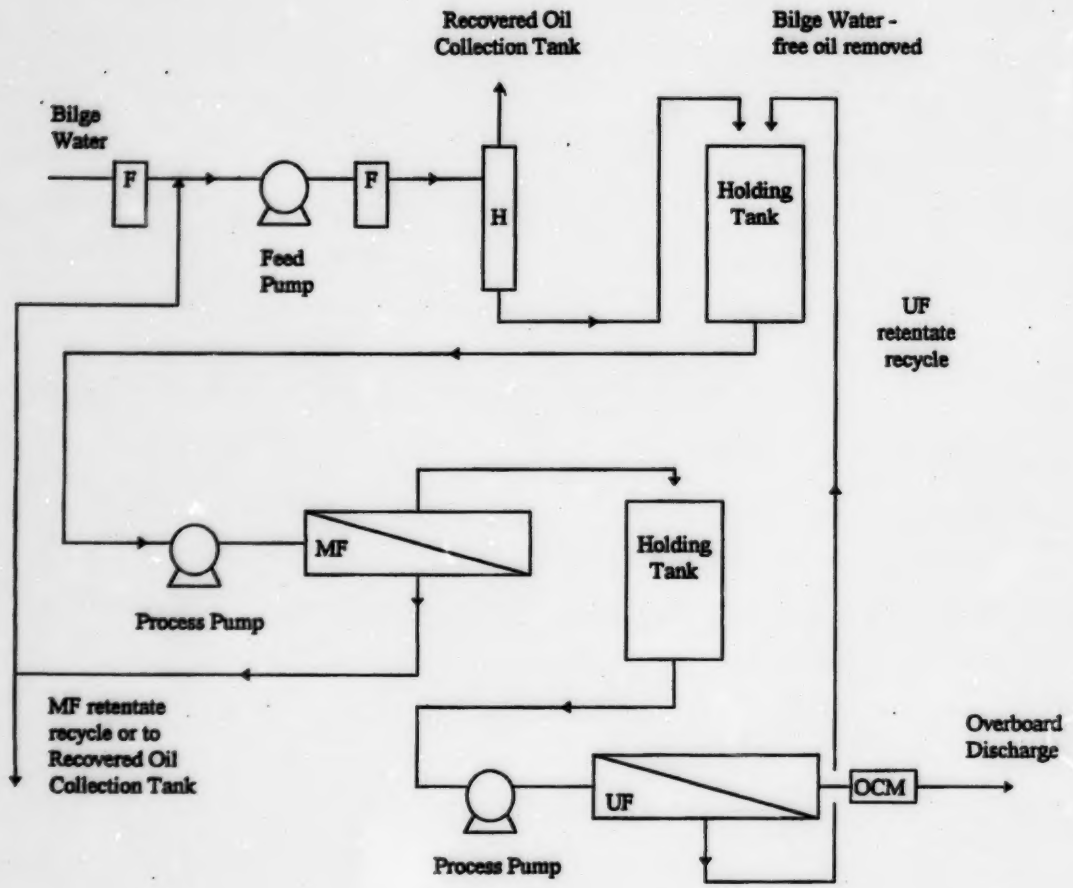

Figure 9: OWS System with Hydrocyclone pre-treatment, Microfiltration and Ultrafiltration, H- Hydrocyclone, F-coarse filters and OCM- oil content monitor.

9.0 Cost Estimates

Important considerations for any system are the capital and operating costs associated with its equipment. A membrane based OWS treatment system will consist of the following major components:

a. feed pump;

b. coarse filter;

c. hydrocyclone;

d. ultrafiltration membrane module;

e. process pump for the ultrafiltration membrane;

f. oil content monitor;

g. control system; and

h. possibly a microfiltration coalescing membrane and a nanofiltration polishing membrane module, each requiring their own pump.

The operating (i.e. maintenance) costs will not be discussed here as these costs will be completely dependent upon the system's reliability and the ability of ship's staffs to efficiently operate the system - factors that are as yet undetermined. However, it would be expected that the system pumps and membranes would require the major of maintenance costs.

With respect to the capital costs of the major components the following are the estimates for the non-membrane components (estimates were obtained from the Canadian Forces Supply System Database and discussions with suppliers):

a. feed pump - MOYNO (positive displacement - to reduce mechanical emulsions) pump - $3,750;

b. coarse filter - $250;

c. hydrocyclone - $9,750 [61];

d. process (centrifugal) pump - $1,000

e. oil content monitor - $7,000; and

f. control system - approximately $20,000, depending on the level of automation required.

Discussions with membrane suppliers revealed that a ceramic ultrafiltration module will cost approximately $11,500 (US), complete with a stainless steel housing. Accordingly, membrane replacement will be approximately $8,000 (US) - the frequency of which is yet unknown as stated above.

If a microfiltration membrane and/or nanofiltration membrane are also incorporated into the system these could be polymeric membranes. This is because the microfiltration membrane would be used to coalesce the oil and therefore the advantage of reduced fouling achieved with the ceramic membrane is unwarranted and the nanofiltration membrane would see little oil as it would be employed as a polishing membrane. Discussions with various suppliers has revealed that polymeric membranes cost approximately $1,000 plus a membrane housing - total cost of approximately $4,000-$5,000. While the maintenance cost are unknown it would be expected that the maintenance cost associated with the microfiltration membrane would be quite high due to its heavy contact with oils and greases and those for the nanofiltration membrane would be low due to its minimal contact with oils and greases.

10.0 Experimental Testing

The earlier sections of this report have identified what considerations should be made when designing a membrane based naval OWS system and what factors will affect its performance. It is now intended to summarize these factors, identify their importance for further study and describe what further information should be determined regarding these factors.

10.1 Experimental Factors

As seen there are many factors which can affect the performance of a naval OWS system. These factors can be divided into two broad categories: those directly related to the membrane and those which are imposed by the design and operation of the treatment system. The factors are:

Membrane related:

a. membrane pore size;
b. operating (transmembrane) pressure;
c. cross-flow velocity;
d. temperature;
e. concentration factor;

Treatment system related:

a. pre and post treatment;
b. backpulsing and cross-flow velocity; and
c. membrane cleaning.

10.2 Importance

Due to the unpredictability of and lack of studies done on bilge water there is little direct information available for any of these factors. However, the factors which are directly related to the membrane are reasonably easy to test for and when

determined can provide a useful guide for the shipborne operation of an OWS. Those that are a consequence of the treatment system design will be somewhat more difficult to determine, but will have a great impact on the OWS unit and on its performance.

For the membrane related factors the two most important to examine are the membrane pore size and the maximum oil/grease concentration that the membrane will tolerate. (Note: It was identified, earlier in this report, that ceramic membranes rather than polymeric ones were more robust and better able to handle the demands associated with oil-water mixtures.) These two factors are considered the most important because it is the membrane pore size (i.e. the tightness of the membrane) that will determine how much rejection of oil and grease will occur and the maximum oil/grease concentration is critical to determine how much separation/bilge water concentration will result. The optimal operating pressure and cross-flow velocities are important, but should be determined once the best membrane pore size has been identified. Studies on the effect of temperature will highlight variations in performance in the operation of the OWS. However, it is impractical to even considered altering bilge water temperature as it is controlled by the indirect contact with the surrounding body of water that a ship transits.

While it is important to know the optimal performance criteria of the membrane, the ability for the system to be able to work and for it to work within the constraints of being used by sailors will be determined by examination of the treatment factors.

With respect to pre-treatment a coarse filter and hydrocyclone are essential to ensure that the membrane is not exposed to excessive solid contaminants and free oil and as such should be implemented into the system. The coarse filter will merely remove large particles from the system and therefore requires no testing. Hydrocyclone testing may be warranted to determine how much oil it can remove and more importantly what size of oil droplet/emulsion it can remove. The hydrocyclone will be particularly important in the event that a "slug of oil" makes it way through the

system - i.e. the hydrocyclone should ensure that the membrane does not see this slug. The final pre-treatment method that should be examined is the use of a microfiltration membrane to coalesce emulsified oil. As one of the primary concerns with the operation of a membrane based system is the possible fouling due to oil and grease methods which can lead to reductions in oil and grease exposure to the main membrane are highly warranted.

For post-treatment it may be necessary to install a very tight ultrafiltration or a nanofiltration membrane after the main MF or UF membrane. This requirement will be based upon the results from the main ultrafiltration membrane (i.e. can it achieve 5 ppm) and the areas that ships will transit (eg: the zero oil discharge is permitted in the arctic). The requirement for a nanofiltration polishing membrane will be determined from tests on the effectiveness of the main ultrafiltration membrane.

To limit the effects of membrane fouling and thereby to reduce the requirement of chemical cleaning the benefits and optimization associated with backpulsing and cross-flow velocity surges should be examined. As detailed, these two techniques will lift and remove the foulants from the membrane surface and do not involve system shut down. Specifically the optimal frequency of backpulsing time and pressure and surge cross-flow velocity should be determined. This should be addressed once the optimal membrane has been selected. With the membrane selected the backpulse and cross-flow velocity can be altered over successive runs to determine their optimal settings.

Despite the benefits of pre-treatment and backpulsing and cross-flow surges it will still be necessary to clean the membrane. Accordingly a cleaning regime should be optimized. Again, the cleaning should be addressed when the optimal membrane has been selected. Experiments can be run whereby the membrane is operated until it is fouled and then cleaning procedures can be conducted to the membrane to determine if initial flux is re-achieved.

Accordingly the following are the factors which should be tested and their relative importance:

a. membrane pore size - mandatory;

b. operating pressure - mandatory - depends on membrane;

c. cross-flow velocity - mandatory - depends on membrane;

d. temperature - mandatory;

e. maximum tolerable oil concentration - mandatory;

f. hydrocyclone - highly recommended;

g. microfiltration (coalescing) membrane - highly recommended;

h. polishing membrane - recommended - dependant upon oil rejection rate of ultrafiltration membrane;

i. backpulsing and cross-flow velocity surges - mandatory - as it is expected that fouling will be the major problem experienced; and

j. cleaning regime - mandatory - as it is expected that fouling will be the major problem experienced.

10.3 Experimentation

As described in section 10.1 the characteristics of the OWS system depend on two major factors - those attributable to the membrane and those attributable to the system. It is on these two major factors that the experimentation is divided. The first set of tests should focus on membrane selection and the determination of its optimal operating conditions. Once the optimal membrane has been determined the optimal membrane configuration and maintenance should be determined.

For the membrane selection it would be recommended to pre-select a number of membranes for testing. Previous experiments indicate that a ceramic membrane with a pore size of approximately 50 Å would be most appropriate. A large number of membranes from varying manufacturers and of varying sizes (smaller and larger than

50 Å) should be tested. These various membranes should then be challenged, with a synthetic bilge water solution [as per 80], under several transmembrane pressures and cross-flow velocities. It would be expected that each membrane would require experimental runs with a minimum of 4-5 transmembrane pressures and cross-flow velocity values. The purpose of these runs would be to determine the membrane with the best flux, lowest rate of fouling and ability to tolerate the highest oil concentration. These runs could also be conducted at varying temperatures if desired or at a set temperature.

Once the optimal membrane has been selected or the choice has been narrowed to 2-3, testing for the system configuration, temperature and cleaning could commence. It would be beneficial to test more than one membrane in the system configuration as the "optimal" membrane selected from the previous tests may not be the optimal membrane with respect to fouling or cleaning. The major focus of optimizing the system configuration is to extend the durability of the membrane. That is, reduce the membrane's rate of fouling and its subsequent cleaning frequency. The focus of the cleaning will be to ensure that the initial membrane flux can be re-achieved.

The system configuration elements consist of a hydrocyclone and piping for backpulsing and cross-flow velocity surges. The hydrocyclone provides pre-treatment whereas the backpulsing and cross-flow velocity would be used with the ultrafiltration membrane. To test for the value of each of these factors the system should be operated with each element operating with the ultrafiltration membrane to determine the extent of their value to the system.

The purpose of the hydrocyclone is to ensure that free oil does not contact the ultrafiltration membrane. Alternately, successive runs could be conducted with varying quantities of free oil present *in* the feed solution, both using and not using the

hydrocyclone, and holding the transmembrane pressure constant and monitoring the membrane flux.

The theory behind backpulsing and cross-flow velocity surges is that this will result in reduced membrane fouling. Accordingly experimental results can be set up whereby a constant transmembrane pressure is applied, and varying frequencies and strengths of backpulse pressure and cross-flow velocity surges are used while monitoring the membrane flux. This will reveal the effectiveness of this procedure as a greater and higher frequency backpulse and cross-flow should result in reduced membrane fouling and in turn increased membrane flux.

With respect to cleaning, various chemicals could be used and at varying strengths to determine their effectiveness for renewing the membrane's flux. This could be examined by determining the membrane(s) initial water flux and then by determining the membrane's water flux after each cleaning.

If other methods, such as ball cleaning, are practicable for the membrane modules they could also be included in experimental in much the same way as the hydrocyclone and backpulse/cross-flow tests; i.e. determine the difference in membrane efficiency when used and not used.

11.0 Conclusion

The literature contains a reasonable amount of information on oil-water separation using membrane technologies. Based on fouling and cleaning considerations, ceramic membranes appear to be superior to polymeric membranes in the treatment of oily/water mixtures,. References on bilge water separation are scarce and provide little information on the potential pitfalls of using membrane technologies onboard naval ships.

The requirement for a naval OWS system are:

a. achieve environmental regulations:
    i. 15 ppm in international waters,
    ii. 5 ppm in inland waters,
    iii. 0 ppm in the arctic;
b. concentrate bilge water in the range of 15.9X to 27.3X;
c. fit within a space of 1.7m (wide) X 1.0m (deep) X 1.5m (high); and
d. automation sufficient to allow for minimum personnel supervision of the system.

It appears that a membrane based OWS holds the potential of achieving all of the above requirements especially if it contains the following components:

a. pre-treatment, including a course filter and hydrocyclone (for free oil removal);
b. membrane module(s); and
c. appropriate cleaning regime.

The primary membranes used should be ceramic since they are substantially more robust than polymeric and as previously mentioned, are better suited to deal with oil-water solutions. However, a polymeric membrane could be used as a "polishing" or a coalescence membrane if these membranes are required.

This initial work has identified several areas where information is needed to optimize system performance and determine the operational characteristics of membrane systems in the treatment of bilge water aboard HMS ships. These areas are as follows:

a. membrane pore size;
b. operating pressure;
c. cross-flow velocity;
d. temperature;
e. concentration factor;
f. hydrocyclone pre-treatment;
g. membrane coalescence;
h. backpulsing and cross-flow velocity surges; and
i. membrane cleaning.

12.0 Recommendations

A membrane based OWS system holds great promise of achieving environmental discharge regulations and of achieving the naval specific requirements. However, due to complexity of bilge water, the initial capital cost of purchasing and installation of these systems (approximately $3M), the inevitable associated life cycle costs plus the requirement to offer proper shore support for these systems to ships warrants further testing to ensure these systems are operated and supported properly.

The most critical areas of examination for a membrane based OWS system are the membrane pore size, maximum oil concentration that the membrane can tolerate, the effects of backpulsing and cross-flow velocity towards the limiting of membrane fouling and membrane cleaning. Areas warranting further consideration are: effects of temperature on membrane performance and pre-treatment (specifically hydrocyclone efficiency and membrane coalescence).

This testing should focus on optimizing the system which the Navy intends to implement. Therefore a working relationship between DND and Water Technologies International (WTI) of Burlington, Ontario should be established. Using this system as a basis for experimentation it is safe to assume that WTI has expended considerable resources towards optimizing the basic membrane characteristics, such as membrane pore size, operating pressure and cross-flow velocity and thus effort could be focused on the reduction of fouling, the subsequent membrane cleaning regime due to fouling and membrane pre-treatment.

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ANNEX A: Applicable Companies and Internet Websites

The following information is provided as a reference of available membrane manufacturers/ suppliers and organizations plus pertinent websites which can provide useful information regarding membrane technology and/or environmental regulations. These lists are not inclusive, they are merely a summary of the resources used during this membrane review which were found useful.

Membrane Companies:

Ceramem Separations	(781) 899-0467
Desalination Systems	(619) 746-4995
Dupont Separation Systems	(302) 695-5234
Koch Membrane Systems	(508) 657-4250
Millipore Corporation	(617) 275-9200
Osmonics	(404) 892-3175
Rhone-Poulenc	(609) 860-3580
Dow Chemical Company	(517) 636-6786 (403) 239-7844
US Filter	(512) 772-1319 1-800-253-3331
Memtek	(609) 953-1788
Zenon Environmental	(905) 639-6320
Seprotech	(613) 523-1641
Water Technology International (WTI)	(905) 336-4855
US Naval Research Facility c/o Mr. Ivan Caplan	(301) 227-5522

Websites: (www.*)

reachit.com/cwwa	Canadian Water and Wastewater Association
owr.ehnr.state.nc.us	Membrane Filtration Systems for Resource Recovery
chemica.com/membranelinks.htm	Membrane Related WWW Links
buscom.com/membrane/c201.html	C-201 Membrane Technology a new era
buscom.com/membrane/gb112r.html	GB-112R: Inorganic Membranes: Markets, Technologies, Players
tc.gc.ca/canadashippingact	Transport Canada - Canada Shipping Act
ex.inel.gov/comply/sector	American Environmental Protection Agency

ANNEX B: Volumetric Reduction Calculations for Bilge Water

Previous studies carried out on Canadian Navy bilge water production have revealed that on average a Canadian warship produced 2.83 m^3/day of bilge water and the IROQUOIS class of ships produce approximately 3.03 m^3/day [56]. During the process of selecting a membrane based OWS system the Canadian navy reviewed their bilge water storage capacity capability and determined that it would be feasible to store up to 8 m^3 of (concentrated) bilge water over a 30 day period - at which point it would have to be discharged to a shore facility [80]. However, the Canadian Navy also stated its preference to limit this 30 day holding capacity to 5 m^3 of bilge water [80].

Accordingly a simple mass balance reveals that for the Canadian Navy to achieve the above stated bilge water storage capacities the concentration factors listed in the following table are required.

Table B.1 Volumetric Reduction Calculations for Bilge Water

	Average HMC Ship	IROQUOIS Class
Daily Bilge Water Production	2.83 m^3/day	3.03 m^3/day
30 Day Bilge Water Production	84.9 m^3	90.9 m^3
Minimum Required Concentration Factor (=30 day production/8 m^3)	10.6	11.4
Preferred Concentration Factor (=30 day production/5 m^3)	17.0	18.2
Required Concentration Factor (based on 50% margin of error)		
Minimum Concentration Factor	15.9	17.0
Preferred Concentration Factor	25.5	27.3

Annex C: Membranes Used for Oily - water separations

Table C.1 Membrane studies for the removal of oil from either bilge, oil field produced or oily water.

WATER	MEMBRANE		EFFLUENT	REMARKS
	Type	Pore Size/MWCO	(TOG)	
Produced	Ceramic	0.8 m	< 10 ppm	[71] US Filter (Membralux) Paper also identifies other membranes suitable for oily water treatment ranging from 0.005-5 microns/3K-200K
Oily	Polymeric	70 000 - 100 000	< 1 ppm	[58] Zenon - Polyvinylidene flouride
Oily	Polymeric	70 000 - 110 000	< 5 ppm	[35] various polymeric (polyvinyl chloride, polyacrylonitrile and cellulose acetate)
Produced	Ceramic	0.2 - 0.8 m	2 - 8.8 ppm	[14] US Filter Membralux membranes
Oily	Ceramic	300 000/0.2 m	0	[21,47] Tech-Sep M9 Carbosep membrane. Article stated that this membrane was a "total barrier" for hydrocarbons. The MWCO seems rather high.
Oily	Polymeric	10 000	0.9 ppm	[48] treated a low oil content oily water
Produced	Polymeric	100 000	95% oil reduction	[5] membrane was polyvinyldifluoride (PVDF)
Oily	Polymeric	0.45 m 0.1 m	n/a	Millipore Gelman
	Ceramic	0.1 m 0.1 m		Ceramesh Membralux [39] Study compared membranes
Oily	Ceramic	0.02 m 0.05 m 0.1 m	80-90% separation	[20] Membralux membranes used - process was asphaltene separation from crude oil
Oily	Polymeric	100 000	5 ppm	[45] Hoechst-werk KALLE polysulphone membrane
Oily	Polymeric	10 000/38 30 000/47	95% reduction	[34] Amicon YM10 & YM30 membranes.
Produced	Ceramic	0.2 m 0.5 m 0.8 m	5-9 ppm	[29]
Oily	Polymeric	6 000 - 100 000	<10 ppm	[30]various membranes were tested with varying results

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In response to increasingly stringent environmental regulations the Canadian Navy has chosen to replace the currently fitted SAREX coalescing Oily Water Separation (OWS) System with a more robust and effective system. After reviewing the available technologies Director General Maritime Engineering Project Management/Director Marine System Support 4 concluded that a membrane based OWS system would provide the best solution for bilge water treatment. Accordingly, after soliciting bids from various companies a contract has been let with Water Technologies International of Burlington, Ontario to provide 16 such systems to the Canadian Navy over the next three years.

While a membrane based system can meet all naval (compactness, automation and operational effectiveness) and environmental requirements it is anticipated that some difficulties will be encountered in placing a new system aboard HMC Ships. Thus, it is prudent to study the system in order to identify and understand its optimal performance and attempt to anticipate any difficulties that may be experienced with its operation. To optimize the system performance the following parameters warrant study: membrane pore size, operating pressure, cross-flow velocity, the frequency and level of backpulse pressure and cross-flow velocity surges. The effects of temperature and the presence of fine particles in the bilge water are also to be studied. It is anticipated that the major shortcoming with a membrane based OWS will be caused by oil and grease fouling the membrane. While it may be possible to reduce the risk of fouling the membrane will still foul. Accordingly an effective cleaning regime should be developed. This regime could include chemical and/or mechanical cleaning.

With the proper understanding of the capabilities and limitations associated with a membrane based OWS system the Canadian Navy should be able to adhere to all environmental regulations pertaining to oily water discharge while not being saddled with an operator intensive system. With the proper commitment the Canadian Navy can once again demonstrate its innovativeness and develop a world leading engineering solution to a problem of concern to North American and European navies.

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